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Process for the preparation of a light-stable  
lubricating oil

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## SPECIFICATION

## Process for the preparation of a light-stable lubricating oil

5 The invention relates to a process for the preparation of a light-stable lubricating oil.

Lubricating oils can be prepared by treating waxy mineral oil fractions with hydrogen in the presence of a catalyst containing one or more metals (and/or compounds thereof) of Group VI and/or Group VIII of the Periodic Table of Elements at elevated temperatures.

The lubricating oils thus obtained often lack sufficient anti-oxidant properties, and to overcome this drawback the oils are conveniently treated in a subsequent second step with hydrogen in the presence of the same or a similar catalyst at a lower temperature than in the first step. The lubricating oils thus obtained have attractive properties in many respects, but they have an unattractive light stability, which means that when exposed to light a haze develops and sludge is formed in a couple of days.

It has now been found that the light stability of these lubricating oils can be tremendously improved by contacting them in the presence of hydrogen with a catalyst which contains one or more metals (and/or compounds thereof) of Group VI and/or Group VIII of the Periodic Table of Elements at a lower temperature than the temperature used in the second step mentioned above.

According to the invention there is provided a process for the preparation of a light-stable lubricating oil which comprises contacting a waxy mineral oil fraction in the presence of hydrogen with one or more supported catalysts containing one or more metals (and/or compounds thereof) of Group VI and/or Group VIII of the Periodic Table of Elements in three subsequent zones, the temperature in the first zone being from 350 to 450°C, the temperature in the second zone being from 300 to 350°C and the temperature in the third zone being from 200 to 325°C, the temperature in the second and third zone being at least 20°C lower than that in the preceding zone.

The waxy mineral oil fraction to be used as starting material for the process of the present invention may be a distillate fraction recovered by vacuum distillation from a residual oil fraction obtained by atmospheric distillation of a mineral oil. The boiling range of such a vacuum distillate is usually from 350°C to 550°C. Residual fractions, in particular a de-asphalted residue of a vacuum distillation, are also very suitable. Waxes obtained by dewaxing of a mineral oil fraction, e.g. slack waxes, may also be used as starting material.

The supported catalyst to be used in the three zones may be the same or different. Examples of suitable supports for the present catalysts are amorphous oxides of elements of Groups II, III and IV of the Periodic Table of Elements, such as silica, alumina, zirconia, thorina and boria, as well as mixtures of these oxides, such as silica-alumina, silica-magnesia and silica-zirconia. Preference is given to catalysts comprising as carrier material alumina. It is further preferred that the catalysts should have a pore volume of from 0.2 to 0.8 ml/g and a surface area of from 50 to 250 m<sup>2</sup>/g.

The catalysts very suitably contain at least one compound of a metal of Group VI of the Periodic Table of Elements, in particular molybdenum or tungsten, and at least one compound of a metal of Group VIII of the Periodic Table of Elements, in particular nickel or cobalt. A metal or a compound thereof of the platinum Group may also be used.

The metals may be incorporated into the present catalysts by any one of the techniques for the preparation of multi-component supported catalysts well known in the art. The metals are preferably incorporated into the catalysts by co-impregnation of a carrier in one or more steps with an aqueous solution comprising one or more nickel and/or cobalt compounds (nickel compounds being preferred) and one or more molybdenum and/or tungsten compounds, followed by drying and calcining. If the impregnation is carried out in several steps, the material may be dried and calcined between the successive impregnation steps.

The catalysts may also be prepared by incorporating the metals into an alumina hydrogel, and drying and calcining the composition, e.g., as described in French patent specification No. 7,441,351.

Preferably, catalysts are applied which comprise from 1-15%w, in particular 2-10%w nickel, and either 5-20%w molybdenum or 15-35%w tungsten.

Very suitably the catalysts also comprise a compound of phosphorus and/or fluorine. These elements may be incorporated during impregnation of the carrier with the metal compounds concerned, or they may be incorporated into an alumina hydrogel together with the metals. Fluorine may also very suitably be incorporated into the catalyst by in-situ fluorination which may be carried out by adding a suitable fluorine compound, such as O-fluoro toluene or difluoro ethane to the gas and/or liquid stream which is passed over the catalyst.

The metals may be present on the carrier either as such or as metal oxides or metal sulphides. The catalysts are preferably used in their sulphidic form. Sulphidation of the catalysts may be effected by any one of the techniques for sulphidation of catalysts well known in the art. Sulphidation may, for instance, be carried out by contacting the catalysts with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butyl mercaptan. Sulphidation may also be carried out by contacting the catalyst with hydrogen and a sulphur-containing hydro-carbon oil, such as a sulphur-containing kerosene or gas oil.

The three subsequent zones with different temperatures in which the waxy mineral oil fraction is to be contacted with a catalyst may be present in one reactor, but it is also possible that for two zones or for each zone a separate reactor is used. The effluent from a zone may be used as such as feed material for the next

zone, but it is also possible to remove certain components from the said effluent (e.g., light components by topping) before it is fed to the next zone.

The temperature applied in the third zone is of prime importance for the daylight stability of the oil to be achieved, and very conveniently is to be determined experimentally for any given oil and chosen catalyst. In general, temperatures from 250°C to 300°C (e.g., up to 310°C) are very suitable.

The hydrogen to be used in the process according to the invention may be pure hydrogen, but this is not necessary. A gas with a hydrogen content of 70% of more by volume is perfectly suitable. In practice it will be preferable to use a hydrogen-containing gas originating from a catalytic reforming plant. Such a gas not only has a high hydrogen content but also contains low-boiling hydrocarbons, for example methane and a small quantity of propane.

The pressure to be used in the process according to the invention may vary between wide limits; the pressure need not be the same in each zone. Pressures lower than 50 bar are less desirable since they reduce the life of the catalysts. Pressures above 250 bar would require costly installations. It is preferable to use pressures from 100 to 200 bar.

The liquid hourly space velocity and the hydrogen/oil ratios may likewise be selected between wide limits in each zone. Very suitable liquid hourly space velocities are from 0.3 to 10, in particular between 0.5 and 5 kg of oil per litre of catalyst. The hydrogen/oil ratio is very suitably from 100 to 5000 standard litres per kg of oil.

From the effluent of the third zone light products (if present) are removed by distillation, and if needed this effluent is dewaxed, in order to obtain the desired lubricating oil which may be used as a component of a lubricating oil composition. Such a composition may contain lubricating oils prepared along the same or different routes from different feedstocks and/or additives in order to improve its properties.

As examples of additives may be mentioned light-stability improvers, which may be used to improve the light stability still further (e.g., 3,3', 5,5'-tetra-tertiary-butyl-4,4'-diphenylquinone), anti-oxidants, viscosity index improvers, detergents, anti-wear extreme pressure additives and pour-point depressants.

#### EXAMPLES

A waxy distillate obtained by distillation from a Middle East crude was contacted at a hydrogen pressure of 140 bar with a catalyst comprising 20%w MoO<sub>3</sub>, 6.5%w NiO, 4.0%w P<sub>2</sub>O<sub>5</sub>, 69.5%w Al<sub>2</sub>O<sub>3</sub>, fluorinated to a fluorine content of 2.5%w, at a temperature of 330°C, a space velocity of 1 kg/h and a hydrogen/oil ratio of 1500 Nl/kg. The product obtained was subsequently contacted at the same hydrogen pressure, space velocity and hydrogen rate with a catalyst comprising 18.7%w MoO<sub>3</sub>, 3.8%w NiO, 5%w P<sub>2</sub>O<sub>5</sub>, 72.5%w Al<sub>2</sub>O<sub>3</sub>, fluorinated to a fluorine content of 2.5%w, at a temperature of 330°C. The product obtained was topped, dewaxed. It had a viscosity index of 96.5, a V<sub>K210</sub> of 11.69 cS, and a daylight stability of 2 days.

The daylight stability is determined as follows:

ASTM pour-point test tubes containing 30 g of the oil are placed in a compartment maintained at 35 ± 0.5°C. The test tubes are then irradiated by two fluorescent tubes (TL 40W/57) and the times taken for sludge formation to occur in the oils noted.

This oil was contacted in the presence of hydrogen with several catalysts at several temperatures and two pressures, and after topping the daylight stability of the products obtained was determined. The experiments were carried out at a space velocity of 0.9 kg/kg and a hydrogen/oil ratio of 2200 Nl/kg.

The Tables 1 and 2 show the results.

Table I  
Pressure 140 bar

Catalyst	Temperature, °C						
	200	225	250	275	300	325	350
1	8	9	8	10	11	7	7
1 + 2.8%W F	9	10	10	11	11	9	7
2	6	8	9	11	11	8	8
2 + 1.8%W F	9	7	13	13	8	6	—
3	8	9	10	10	13	9	—
3 + 2.0%W F	9	10	9	10	14	8	—
4	7	8	9	12	8	8	—

Table 2  
Pressure 110 bar

	Temperature, °C					
	200	225	275	300	325	350
Catalyst 3	7	7	9	9	8	8

Catalyst 1 is an alumina-based catalyst containing 6.5%w NiO and 29.5%w WO<sub>3</sub>. It has a pore volume of 0.65 ml/g and a surface area of 211 m<sup>2</sup>/g.

Catalyst 2 is an alumina-based catalyst containing 6.5%w NiO, 20.0%w MoO<sub>3</sub> and 4.0%w P<sub>2</sub>O<sub>5</sub>. The pore volume is 0.38 ml/g and the surface area 147 m<sup>2</sup>/g.

5 Catalyst 3 is an alumina-based catalyst containing 3.8%w NiO, 18.9%w MoO<sub>3</sub> and 5.7%w P<sub>2</sub>O<sub>5</sub>. The pore volume is 0.54 ml/g and the surface area 201 m<sup>2</sup>/g. 5

Catalyst 4 is an alumina-based catalyst containing 6.5%w NiO, 30%w WO<sub>3</sub> and 6%w B<sub>2</sub>O<sub>3</sub>. The pore volume is 0.28 ml/g and the surface area 102 m<sup>2</sup>/g.

All catalysts are sulphided before use by contacting them with a gas oil and hydrogen under reaction 10 conditions. The fluorided catalysts were prepared by incorporating 250 ppm F as o-fluoro-toluene in the feed 10 until the equilibrium concentration of fluorine in the catalyst had been established.

It can be seen from the Tables that the optimum temperatures in the third zone for improving daylight stability are from about 250° to about 300°C.

## 15 CLAIMS 15

1. A process for the preparation of a light-stable lubricating oil which comprises contacting a waxy mineral oil fraction in the presence of hydrogen with one or more supported catalysts containing one or more metals (and/or compounds thereof) of Group VI and/or Group VIII of the Periodic Table of Elements in 20 three subsequent zones, the temperature in the first zone being from 350 to 450°C, the temperature in the second zone being from 310 to 350°C and the temperature in the third zone being from 200 to 325°C, the temperature in the second and third zone being at least 20°C lower than that in the preceding zone. 20
2. A process according to claim 1, in which the support of the catalyst(s) is alumina.
- 25 3. A process according to claim 1 or 2, in which the catalysts have a pore volume of from 0.2 to 0.8 ml/g. 25
4. A process according to any one of the preceding claims, in which the catalysts have a surface area of from 50 to 250 m<sup>2</sup>/g.
5. A process according to any one of the preceding claims, in which the metals of Group VI of the Periodic Table of Elements are molybdenum or tungsten.
- 30 6. A process according to any one of the preceding claims, in which the metals of Group VIII of the Periodic Table of Elements are cobalt or nickel. 30
7. A process according to claim 6, in which the said metal is nickel.
8. A process according to any one of the preceding claims, in which the catalysts comprise from 1-15%w, and either 5-20% w molybdenum or 15-35% w tungsten.
- 35 9. A process according to any one of the preceding claims, in which the temperature in the third zone is 35 from 250°C to 300°C.
10. A process according to any one of the preceding claims, in which the pressure is from 100 to 200 bar
11. A process according to any one of the preceding claims, in which the liquid hourly space velocity is 40 from 0.1 to 10 kg of oil per litre of catalyst and the hydrogen/oil ratio from 100 to 5000 litres per kg 40 of oil.
12. A process according to claim 1, substantially as described, with special reference to the Examples.
13. Lubricating oils obtained according to the process of any one of claims 1-12.
14. Lubricating oil compositions comprising a lubricating oil according to claim 13.